Response to Letter to the Editor

Dear Dr. Frant,

Thank you for your valuable contributions on our paper. "Preparation of a new solid state fluoride ion selective electrode and application". You raise some interesting issues.

Here are the responses. For completeness, I include relevant earlier correspondence with you about our electrode.

(1) Your comment on your former letter:

"There still seems to be some question about the effect of pH on fluoride activity. The pK for HF is 3.164 at 0 dilution and 25°. There is no data for 0.1 M NaNO$_3$, but at 0.5 M NaNO$_3$ the pK is 2.88 at the same temperature (Salomon and Stevenson, J. Chem. Eng. Data 19, 42). At a pK of 2.88, the free fluoride in the 10^{-3} M solution you used would be about:

pH	Free fluoride
1	1.3×10^{-5}
2	1.2×10^{-4}
3	5.7×10^{-4}
4	9.3×10^{-4}
5	9.9×10^{-4}

If I use a pK closer to what be expected for 0.1 M NaNO$_3$, say 2.93, the results hardly change.

pH	Free fluoride
1	1.2×10^{-5}
2	1.1×10^{-4}
3	5.4×10^{-4}
4	9.2×10^{-4}
5	9.9×10^{-4}

Either way, there should be a two-decade change in fluoride activity in going from pH 1 to pH 5, and if the electrode is responding to fluoride activity it should have shown that change."

Your second comment on the same subject, on your last letter:

"However, there are some serious inconsistencies in the data which I could not resolve.

For example, Fig. 3 in the paper shows the response of the fluoride electrode as a function of pH. At "various fluoride concentrations" (not specified in the paper), and in 0.1 M NaNO$_3$, the change in potential "from pH 1 to 8" . . . "was only 1–2 mV per pH unit". However, the pKa for HF is 3.164 (1) at zero dilution and 2.88 (2) at 0.5 M NaNO$_3$. Assuming that the only complex between H$^+$ and F$^-$ is HF (no HF^{2-} at the fluoride levels in the paper), either value of the pKa gives a calculated change in fluoride activity over the pH range 1–5 of nearly 5 orders of magnitude. Even for the reported non-Nernstian slope of 26 mV, that would be a change of over 100 mV. The electrode does not seem to be responding to fluoride activity."

Answer to both of these comments:

According to your former calculation the fluoride concentration (if it were at the beginning 10^{-3} M) will increase 100 times (from 1.3×10^{-5} to 9.9×10^{-4} M) for a pH change of 1–5. (It is not 5 orders of magnitude. I believe your original calculations were correct.) Our pH was about 7, since the electrolyte was 0.1 M NaNO$_3$. In our manuscript Section 3.3 this experiment with fluoride was made in order to see the pH effect on slope by the additions of F ion. That means at each pH the slope for fluoride was measured. After this, it was found that the slope was high in the presence of NaNO$_3$ and the solution pH was about 6–7. We did not use high pH values, since the potential changes with pH. At low pH values the response (the slope) for F was low.

(2) Your comment on:

"In the alkaline region, pH 7–13, where the fluoride activity does not change (except for ionic strength effects) the reported electrode readings *increase* by about 70 mV. Here again, the electrode does not appear to be responding to fluoride activity. (The shape of the entire curve and the increasingly negative readings on the alkaline side look very much like the pH curves obtained with divalent cations, where they precipitate or complex with hydroxide ions, but are stable in acid.)"

Answer to this comment:

Many scientists have used Cu$_2$S in their electrodes, does that mean all of these electrodes were measuring copper at high pH values? This may be true with these electrodes at pH values larger than 9, since only at high pHs it is possible that copper, formed because of slight dissolution of Cu$_2$S, may be oxidized to form the OH complex of Cu(II). The potential becomes more negative with increasing pH, which means an anion concentration is increasing. We worked at about pH 7, with NaNO$_3$ not at higher pH, and there is no such problem.

(3) Your comment on:

"Nonetheless, the paper reports a calibration curve for fluoride over the range of 10^{-1} to 10^{-6} M. The pH of the calibration curve is not specified. Measurements on spring and tap water, based on using standard addition are also reported. For standard addition, the problem is that two fluoride activity measurements are needed for the calculation that (for their electrode) would typically differ by about 8 mV. It is difficult to understand how an electrode that was unresponsive to orders of magnitude changes in fluoride activity due to complexation with hydrogen ion, could have the necessary precision for standard addition (or for that matter, to generate a calibration curve.)"

Answer to this comment:

The working pH is about 6–7 since 0.1 M NaNO$_3$ was used in order to protect the ionic strength.

For the determination of fluoride in spring and water samples first the potential of 0.1 M NaNO$_3$ was measured, then 2–3 times the sample was added until a reasonable change (10–25 mV), in potential was measured, then at least two standard additions were

made, and potential changes were measured. The standard additions were made again so that each time the potential change was large enough (15–25 mV) to make it possible for accurate determination. Then calculations are made accordingly. Thus, why the potential change would be 8 mV (as you claim) is not clear.

(4) Your comment on:

"There is nothing obvious in the electrode membrane composition that would suggest a response to fluoride ion. All of the solid state ion-selective electrodes that I am familiar with contain an ionic conductor to which the electrode responds directly or through a solubility product relationship with the ionic conductor (e.g., electrodes for $S^=$: Ag_2S, Cu^{2+}: Ag_2S/CuS, etc.). The membrane in the Somer et al., paper contains the ionic conductor Ag_2S, but the only source of fluoride ions is CaF_2, which is not an ionic conductor and is soluble enough to yield a fluoride level of *around 0.001 M F^-*. Further, both AgF and CaS are soluble compounds that could not affect the dissociation of Ag_2S."

Answer to this comment:

You mentioned that, for (sulfur) $S^=$ only Ag_2S, for Cu only Ag_2S and CuS had to be used, but previous literature mentions about electrodes selective for sulfate ($SO_4^=$) where $PbSO_4$, PbS, Ag_2S and Cu_2S were used, for Cd: CdS and Ag_2S, for Pb: PbS and Ag_2S used

Some references:

G.A. Rechnitz, Anal. Chem. 41 (1969) 12–109; M.S. Mohan, G.A. Rechnitz, Anal. Chem. 45 (1973) 1323–1326; F. Pal, K. Toth, E. Pungor, M. Farkas-Jhanke, H. Ebel, M.F. Ebel, Anal. Chim. Acta 180 (1986) 313.

There are also some electrodes in the literature, as mentioned in our paper, sensitive to fluoride, where fluorides of Th, fluorides of rare earth elements and CaF_2 were used.

A.M.U. Macdonald, K. Toth, Anal. Chim. Acta 41 (1968) 99–106.

I do not agree with your comment on "the only source of fluoride ion is CaF_2, which is not an ionic conductor and is soluble enough to yield a fluoride level of around 0.001 M fluoride"

Since:

(a) If it were so, the potential of $NaNO_3$ after the electrode was soaked into $NaNO_3$ would change with time (I would like to notify that no F was added at the beginning). But the potential of our electrode becomes steady immediately (1–2 s) after it is soaked into $NaNO_3$. The potential remains steady for at least 20–30 min. Only after the addition of fluoride, it changes. It needs about 20–30 s for the potential to be steady after each addition of fluoride, which is an indication that CaF_2 does not dissolve.

(b) The electrode is not only CaF_2 precipitate, there are also 70% Ag_2S, 10% Cu_2S and the membrane is like a glass after the application of 8000 kg/cm^2 (7760 atm) pressure for several minutes. Thus, it will not dissolve like a CaF_2 precipitate in water.

If there are further comments on our paper I shall be glad to answer them also.

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